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As acrylic fibers are heated in air to induce the stabilization reactions, the tension developed when stabilized at constant length and the instantaneous velocity of stabilizing fibers undergoing continuous processing both depend on the chemical composition, diameter, and orientation of the precursor fiber. An oriented fiber will tend to shrink when heated to the range of 130-160C, and hence will develop tension if restrained at constant length. Although this process has no direct relation to the stabilization process, it

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will influence the instantaneous velocity of the fiber during the later stages of continuous processing. As a fiber held at constant length is heated above 160C the tension developed by entropic relaxation decreases and the fiber starts to undergo the prefatory and sequent reactions of stabilization described in the first paper in this series. If the prefatory reactions are rapid, a rigid structure is quickly established in the fiber and tension again increases rapidly. However, if the prefatory reactions are slow, select portions of the fiber react preferentially and the unreacted portions tend to relax to maintain a temporary quasi-equilibrium tension level. In both cases the fibers shrink at the later stages of stabilization because of chemical reactions. The shape of the tension-time curve is similar to the oxygen-uptake curves: the diffusion-limited mechanism of stabilization produces parabolic curves whereas the reaction-limited mechanism produces linear curves. Because each element of a fiber undergoing continuous pro-cessing is subjected to the same tension at all times, previously oriented fibers first shrink, then stretch, and finally shrink again. These competing processes give rise to a changing instantaneous velocity. Data are presented for fibers of varying chemical composition, diameter, and initial orientation as well as for different conditions of stabilization.

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OXIDATIVE STABILIZATION OF ACRYLIC FIBERS

III.   STABILIZATION DYNAMICS

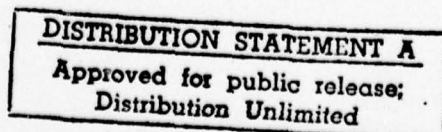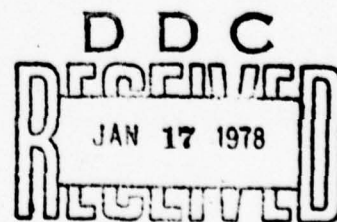S.B. Warner[+], L.H. Peebles, Jr.[*] and D.R. Uhlmann

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ABSTRACT

As acrylic fibers are heated in air to induce the stabilization reactions, the tension developed when stabilized at constant length and the instantaneous velocity of stabilizing fibers undergoing continuous processing both depend on the chemical composition, diameter, and orientation of the precursor fiber. An oriented fiber will tend to shrink when heated to the range of 130-160C, and hence will develop tension if restrained at constant length. Although this process has no direct relation to the stabilization process, it will influence the instantaneous velocity of the fiber during the later stages of continuous processing. As a fiber held at constant length is heated above 160C the tension developed by entropic relaxation decreases and the fiber starts to undergo the prefatory and sequent reactions of stabilization described in the first paper in this series. If the prefatory reactions are rapid, a rigid structure is quickly established in the fiber and tension again increases rapidly. However, if the prefatory reactions are slow, select portions of the fiber react preferentially and the unreacted portions tend to relax to maintain a temporary quasi-equilibrium tension level. In both cases the fibers shrink at the later stages of stabilization because of chemical reactions. The shape of the tension-time curve is similar to the oxygen-uptake curves: the diffusion-limited mechanism of stabilization produces parabolic curves whereas the reaction-limited mechanism produces linear curves. Because each element of a fiber undergoing continuous processing is subjected to the same tension at all times, previously oriented fibers first shrink,

then stretch, and finally shrink again. These competing processes give
rise to a changing instantaneous velocity. Data are presented for fibers
of varying chemical composition, diameter, and initial orientation as
well as for different conditions of stabilization.

I. INTRODUCTION

In the conversion of acrylic fibers to carbon fibers little is
known about how variations in the stabilization process affect the
mechanism of stabilization. Paper I of this series (1) describes the
mechanism in terms of a series of unspecified reactions which lead up
to and include the polymerization of the nitrile groups, called prefatory
reactions, and a series of reactions that follow nitrile polymerization,
called sequent reactions. The difficulty in specifying more precisely
the chemistry of the system stems from the inability to characterize
adequately the stabilized fiber. It is known that oxygen plays an
important role in stabilization, yet it is not known how the added
oxygen is incorporated into the fiber. It is probably present in a
number of different structures; but the percentage of each functional
group is unknown (2). Paper I further suggests that oxidative
stabilization can occur under two different limiting conditions: a
reaction-limited mechanism and a diffusion-limited mechanism.

In the reaction-limited case, both the prefatory and the sequent
reactions proceed slowly throughout the fiber and it darkens uniformly
across the fiber diameter; a thin (500 $\overset{\circ}{A}$) skin is established which
tends to limit the diffusion of oxygen. The overall reaction rate is

limited by the rate of the prefatory reactions, and oxygen uptake proceeds linearly with time.

In the diffusion-limited case, the prefatory reactions either occur rapidly, or are allowed to occur in the absence of oxygen. When oxygen is present, the fiber develops a dark outer mantle or rim. This mantle first darkers progressively at a nearly-constant thickness (about half the fiber radius); and with further treatment time, the mantle moves towards the center of the fiber. It is suggested that during the latter stage, the dark mantle limits the diffusion of oxygen to the core of the fiber and the sequent reactions are occurring at the interfacial regions between skin and core.

In making carbon fibers, the acrylic fibers are usually heat-treated in air under conditions and for sufficient time to allow the fiber to be processed further at higher temperatures. Many studies have been carried out to determine the proper process conditions to improve the quality of the final yarns and to decrease their cost; yet it remains unclear how the process variations affect the chemistry and structure of the stabilized fiber. Two processes have been widely used to achieve stabilization: In one, the fiber is heat treated while constrained to constant or nearly-constant length (3), analogous to a stress-relation experiment. In the other, the fiber is heat-treated while restrained by a constant force, analogous to a creep experiment. Constant force can be maintained either by using a riding pulley (4), by hanging weights from the fiber end (5, 6) or by continuous processing (7) in which the fiber is continuously fed into and removed

from the heat-treatment zone.

Layden (5) suspended a known length of an unspecified acrylic fiber in the center of a furnace and measured either the change in length under various loads or the change in tension. He found that for small loads, as the fiber is heated up to 270°C it initially shrinks, then stretches, then shrinks again; while for larger loads, the process is reversed: as the fiber is heated, it initially stretches, then shrinks, then stretches again and finally breaks.

Watt and Johnson (6) observed a different response when unspecified acrylic fibers were heated at 220°C in air under constant load: at low loads the fibers shrink, while at higher loads the fibers initially stretch and then shrink. In contrast, Fitzer and his colleagues (8-10) reported that only shrinkage occurred when polyacrylonitrile fibers where heated at various temperatures under a constant load. It was also reported, however, that under continuous process conditions, the fibers initially increased in length and later shrank.

Bahl and Manocha (11) observed the effects of oxidizing atmosphere and temperature on homopolymers and unspecified copolymers. An initial shrinkage was observed which was independent of atmosphere and could be eliminated with sufficient load. A secondary shrinkage was also observed and was dependent on the oxidizer content. Whereas Watt and Johnson take the position that shrinkage is caused by molecular relaxation, Fitzer and his colleagues and Bahl and Manocha suggest the occurrence of two distinct processes involving respectively a physical

and a chemical mechanism.

The present paper is directed toward clarification of these issues. Both stress relaxation and creep measurements on different fibers will be used to provide insight into the processes of stabilization. The experiments show how information derived from stress relaxation can be used to understand the dynamic behavior of fibers undergoing continuous processing.

II. EXPERIMENTAL PROCEDURE

Heat treatment of the acrylic fibers was carried out in the furnace shown schematically in Fig. 1. Each of the four zones was independently maintained within $\pm$ 1°C of the set temperature by a Eurotherm series 96 controller. To minimize thermal gradients caused by the spacing of the heating elements, the furnace had an internal liner of copper tubing. A slot was milled the entire length of the copper tube so the fiber could be viewed at all times. In some runs, air was provided through the intake port (about 50 cc sec^{-1}); in others, a preheated 5 pct hydrogen forming gas was provided at a high flow rate (about 500 cc sec^{-1}). to the center of the furnace by a small bore copper tubing inserted through the exit port. No attempt was made to use an oxidizing gas other than air. The temperature profile is shown in Fig. 2 for the case where all four zones of the furnace were set at 230°C. This figure illustrates typical temperature ramps at the entrance and exit of the furnace.

The fibers were processed in this furnace in either of two modes:

A. In the stress relaxation mode, a length of fiber was held in the furnace by two fine copper wires. The shrinkage force developed by the fiber was monitored with a Zivy tensiometer as a function of time and temperature. Two nonidealities existed in the operation of this mode. First, the fiber was inserted at 20°C, and the temperature was raised over about 25 minutes to the desired temperature. During this heatup period, the copper wires expand, reducing the shrinkage force. If the fiber shrinks less than 0.4%, a constant or a decreasing tension will be observed during the warmup period. The curves of shrinkage force vs. time have not been corrected for this effect because the total force decrease is the same in all cases, and only the data for the initial time period are affected. The main region of interest is that after thermal equilibrium has been established in the oven.

The second nonideality arises from the mechanism of the Zivy tensiometer, which measures the force by allowing some length change, a maximum of 2.3 pct. for 150 cm. of fiber (corresponding to 100 gms. increase in tension). The fiber is permitted, therefore, to contract slightly with increasing shrinkage force. The maximum shrinkage allowed by the tensiometer is 10% or less of the unrestrained shrinkage reported by Fitzer et al. (9, 10).

B. In the continuous mode (creep mode) of furnace operation, a variable speed godet was used to control the speed of the fiber entering zone 1, and a variable speed synchronous motor connected to a take-up

spool removed the fiber from zone 4. For a given fiber and temperature profile, the tension and the overall strain were determined by the differential motor speed. While operating in this mode, only steady state measurements were made. In order to eliminate fiber breakage during continuous processing, zone 1 was never set higher than 230°C. Therefore, heat treatment at, say, 290°C means zone 1 was at 230°C and the remaining 3 zones at 290°C. When the furnace was operating in this mode, the velocity of the fiber was determined by measuring its instantaneous speed as it underwent stabilization. This was accomplished with a cathetometer and a stopwatch.

Specifications of fibers M, O, D and C used in these investigations are given in Paper I of this series (1). The various deniers of fiber N, a Monsanto experimental acrylic fiber having the same composition as fiber M, were obtained by varying the draw ratio.

III. RESULTS AND DISCUSSION

Shrinkage Force

Data on the dynamic shrinkage force measured for four fibers stabilized at constant length in air are shown in Fig. 3. The differences in behavior observed for the different fibers are striking. As the temperature of the furnace approaches the glass transition temperature, fibers M, O, and C start to shrink and develop tension. The maximum tension is attained in the region about 140-150°C and then declines to a "plateau region". The development of tension at temperatures about 140-150°C is due to entropic recovery of a drawn and quenched material. Fiber D does not develop tension in this region

because it is essentially unoriented (12). Shrinkage tension can be developed in fiber D by drawing it over a hot pin prior to the heat treatment (see, e.g., Fig. 4). The initial development of tension (in the region of the glass transition) can be eliminated from all fibers by heat setting the unrestrained material; further, the maximum tension is regulated by the draw ratio (see, e.g., Fig. 5). Therefore, the behavior of acrylic fibers up to temperatures where color changes begin to occur (180°C) is related to processing details of the precursor fibers, and is not related to the stabilization reactions.

The most important features of Figs. 3 and 4 concern the onset and shape of the second increase in shrinkage force (termed secondary shrinkage). Fig. 6 shows that the incubation time (in the plateau region) and the rate of secondary shrinkage depend on the stabilization temperature for fiber M. All four fibers show a decrease in incubation time and an increase in secondary shrinkage rate with an increase in reaction temperature. More importantly, however, there is a temperature range for each type (and denier) of fiber below which the secondary shrinkage is linear with time and above which it is parabolic. For 1.23 denier Fiber M, this temperature is about 285°C; for 4 denier Fiber C, it is about 185°C. Examination of the cross-sections of these two fibers shows that when the rate of secondary shrinkage is linear, the fiber uniformly changes color through the cross-section area as described in the Introduction. In contrast, when the rate of shrinkage is parabolic, the fiber cross sections are characterized by the two-zone morphology.

The similarity in shape of the curves of secondary shrinkage vs.

time, as well as the complimentary observations of fiber cross-sections suggest a relation between reaction kinetics and secondary shrinkage (1).

Measurements of the shrinkage force during heat treatment of fibers in an inert atmosphere have helped in assessing the mechanism of secondary shrinkage. Considerable difficulty is encountered, however, during heat treatment in an inert atmosphere: At low temperatures (less than 230°C for fiber M) color changes--and hence the reactions--proceed quite slowly, whereas at higher temperatures (in excess of 240°C), increased frequency of fiber breakage is observed because the exothermic reactions proceed in an uncontrolled manner.

The shrinkage force curves of the four fibers on treatment in forming gas at 230°C are shown in Fig. 7. Only at long reaction times, if at all, do fibers M, O, and D show signs of shrinkage. Since the furnace was not completely airtight, this shrinkage may have been related to air leaks and subsequent reaction, even though the fibers did not become black. The rapid increase in secondary shrinkage force for fiber C suggests, however, that oxygen is not essential for shrinkage. When air is leaked into the oven subsequent to substantial prefatory reaction taking place, the fiber becomes black and further increases in tension result, as shown in Fig. 8. This behavior indicates that oxygen catalyzes or participates in the reactions which cause shrinkage.

To complete the case for a direct correlation between secondary shrinkage force and reaction kinetics, it is necessary to explain the incubation period which is present in the tension measurements of fibers M,

O and D but not in their corresponding curves of oxygen uptake. To this end, observations of fiber cross-sections were correlated with the mechanism of stabilization (1). Under conditions in which the rate-limiting step in stabilization is reaction-controlled, both prefatory and oxidative reactions occur slowly, at sites distributed throughout the fiber. Under conditions of diffusion control, on the other hand, prefatory reactions occur relatively rapidly throughout the fiber, and the rate of oxidation is limited by transport of oxygen through the outer oxidized layer. Once temperature is attained, the observed shrinkage of fibers stabilizing with a single-zone cross-section likely results from prefatory reactions as well as the sequent reactions in which oxygen plays a major role. In fibers that stabilize with the characteristic two-zone structure, however, the prefatory reactions are well underway in the time it takes to achieve uniform temperature and the secondary shrinkage results primarily from reactions involving oxygen.

At temperatures above 150°C, all virgin acrylic materials are easily extended: local extension can proceed easily within the acrylic regions in response to shrinkage induced by reactions in nearby volume elements, in contrast, the stabilized material cannot undergo differential extension-shrinkage. When stabilization is reaction-controlled, the prefatory and sequent reactions occur at sites well distributed through the fiber; after a continuum of material capable of bearing and transmitting load is established, realizable shrinkage can be measured and, hence, the incubation time ends. When stabilization is diffusion-

limited, on the other hand, sequent reaction occur at the boundary of the outer layer of the fiber. In this way, shrinkage force is transferred along the fiber at all measurable times and, hence, negligible incubation times are observed.

The effect of fiber denier on the rate of secondary shrinkage for fiber N under conditions of reaction control, shown in Fig. 5, parallel the effect of denier on rate of oxygen uptake: A plot of the secondary shrinkage slope against the reciprocal of the square root of denier leads to a linear relationship. The consequences of this observation, that denier significantly affects the slope of secondary shrinkage via reaction rate, should not be ignored. It suggests, for example, that fibers of similar denier be used in effective comparisons of shrinkage behavior of different types of fibers.

Continuous Processing

When stabilization is achieved by heating a fiber fed continuously into one end of a furnace and removed at nearly the same rate from the other end, the local velocity of the fiber is not single-valued throughout the hot zone. Rather, the fiber responds to the constant force according to its local properties. Fig. 9 shows the behavior of fiber M at steady state in a temperature gradient. There are three distinct regimes of response: first the fiber shrinks, causing an increase in its denier; then it draws; and finally it shrinks again. Due to the expansion and contraction of the fiber diameter, no simple correlation exists between the position-average velocity of the fiber and the average velocity calculated on the basis of (differential)

input and output rates.

To understand this behavior, consider first an ideal elastomer being continuously drawn between two sets of pinch rolls, as shown schematically in Fig. 10A. If the speeds of the pinch rolls are equal, then the instantaneous velocity would be the same throughout the draw zone. If the exit speed is now increased, the elastomer will draw immediately after passing through the first set of rolls, giving rise to the local velocity curve shown in Fig. 10B. If an unoriented semi-crystalline polymer (say 40% crystallinity) is substituted for the elastomer and a suitable temperature gradient is added between the rolls, then (assuming homogeneous drawing occurs), the polymer will begin to draw near the glass transition, T_g. The presence of ordered regions in the polymer and the viscoelastic nature of the material above T_g is expected to extend the range of drawing. The behavior expected for this material is illustrated in Fig. 10C, and that measured for an essentially unoriented fiber D is shown in Fig. 11.

When a previously oriented semicrystalline fiber is subjected to the same temperature gradient and draw ratio described above, it should first decelerate in the vicinity of T_g (region A, Fig. 10D) owing to entropic recovery, then accelerate in region B in order to obtain the final extent of orientation which is greater than the initial amount. The gradient between the input velocity and the minimum velocity should depend on the tension applied to the fiber. If the reoriented semicrystalline fiber now undergoes a high temperature shrinkage-inducing reaction, a velocity profile of the form shown in Fig. 10E is expected. The secondary

shrinkage requires a compensating amount of additional draw; and it
occurs at the region in the threadline where the fiber offers the
least amount of resistance (i.e., in the unreacted acrylic material
after entropic shrinkage and not in the stabilized material) to produce
a maximum in the local velocity trace. Two conditions are shown in 10E:
the solid line would result in the chemical reactions leading to shrinkage
were incomplete whereas the dashed line represents material in which
stabilization is complete before the fiber emerges from the furnace.
The expected behavior shown in Fig. 10E corresponds excellently with
the experimental results shown in Fig. 9 above.

The behavior of fiber D is predicted quite well by the model.
Since this fiber is essentially unoriented, there is no discernable
initial shrinkage. Figs. 12 and 13 show the effect of temperature on
the local velocity for underfeed and overfeed conditions, respectively.
Generally, the amount of draw increases with the amount of secondary
shrinkage. Stabilization itself, however, reduces the deformability
of the material by forming both a ladder polymer and intermolecular
crosslinks. When reaction rates are high, the early formation of products
limits the amount of draw, especially when the oxidation process is
limited by diffusion. This behavior is exemplified by the curve labeled
"290°C" in Fig. 12.

Figs. 12 and 13 also show the effect on the local velocity of varying
the take-up speed (to alter the overall extension). Comparison of
either the 230°C or the 255°C curves in the figures shows that a higher

process draw at a given temperature gives rise to a greater velocity maximum to compensate for the increased output speed.

The effect of temperature on the behavior of 8 denier fiber N is shown in Fig. 14. Once again, high heat treatment temperatures lead to large differences in local velocity. This is a result of additional extension when the fiber is extremely weak to compensate for the enhanced secondary shrinkage.

The apparent slight dip in the velocity of some fibers just prior to emergence from the furnace (see, e.g., Fig. 13) results from details of the experiment. The velocity measured at 400 cm was measured within the furnace, whereas the final velocity was actually measured at the take up roll, not at 425 cm. The fiber is cold when it arrives at the take up roll and has a significant moisture regain, which causes the fiber to extend longitudinally (13, 14). The dip in velocity therefore occurs outside of the furnace as the fiber temperature falls below 100°C. The magnitude of the dip is greater when operation is conducted under humid conditions.

The effects of process variables on the local velocity traces may be briefly summarized as follows: Entropic shrinkage produces a velocity minimum, and stabilization reactions produce a maximum, in velocity. Increasing the temperature generally depresses the minimum by lowering the overall tension and raises the maximum by promoting secondary shrinkage; the latter trend can be reversed at very high reaction temperatures by the occurrence of intermolecular reactions during extension. Increasing the denier decreases the rate, but increases the

potential amount, of secondary shrinkage.

IV. CONCLUSIONS

Two stabilization processes have been examined in detail: stabilization during which the fiber length is invariant (batch processing) and stabilization during which the fiber tension is invariant (continuous processing). Using the former (batch) process, two regimes of shrinkage force have been noted. During heatup, the fiber tension rises as the glass transition is exceeded. This is associated with entropic recovery. Again at a later time, related directly to stabilization kinetics, the tension rises because of chemical reactions occurring in the fibers. Specifically, the shrinkage reactions can occur in the absence of an oxidizing gas, but oxygen present in the atmosphere has an accelerating effect on the rise in tension. A correlation between the development of shrinkage forces and the mechanism of stabilization has been demonstrated.

Under conditions of continuous processing, the velocity of the fiber varies with position in the reaction furnace. The precise form of the local velocity trace of a given fiber undergoing continuous processing is a function of the overfeed, the reaction temperature, the treatment time and, of course, the precursor and its draw history. When the overfeed is small or zero, fibers generally undergo an initial marked redrawing, but shrink during late stages of stabilization in response to stresses generated by chemical reactions. Again a correlation exists between the local velocity traces and the mechanism of fiber stabilization.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Fig. 1   Schematic of Stabilization Furnace

Fig. 2   Temperature Profile in Stabilization Furnace with Temperature
Set at 230°C.

Fig. 3   Shrinkage Force Curves for Acrylic Fibers Heat Treated in Air.

Fig. 4   Effect of Draw on the Entropic Shrinkage of Fiber D heat
Treated in air at 230°C.

Fig. 5   Effect of Denier on the Development of Tension During the
Heat Treatment of fiber N at 230°C.

Fig. 6   Effect of Temperature on the Shrinkage Force Curve for Fiber M
Heat Treated in Air.

Fig. 7   Development of Shrinkage Force in Acrylic Fibers with Heat
Treatment Time in an Inert Atmosphere.

Fig. 8   Effect of Change from Inert to Oxidizing Atmosphere on the
Shrinkage Force of Fiber C.

Fig. 9   Local Velocity of Fiber M Stabilizing in Air in a Temperature
Gradient

Fig. 10 Predicted Behavior of Model Fibers Under Conditions of
Continuous Processing.

Fig. 11 Local Velocity of Fiber D at 180°C.

Fig. 12 Effect of Temperature on Local Velocity of Fiber D when Underfeed
gives an overall extension. (Quotation marks about the temperature
indicate that the first thermal zone was set at 230C and the remaining
zones at the indicated temperature.)

Fig. 13 Effect of Temperature on Local Velocity of Fiber D when Overfeed

gives an overall shrinkage.

Fig. 14 Effect of Temperature on the Local Velocity of 8 Denier Fiber N

Air inlet

Inner pyrex tube nichrome wrapped

Outer pyrex wall

ZONE 1

Copper tube

ZONE 2

Silicone rubber

ZONE 3

Thermocouples

ZONE 4

III-13